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Cationic Palladium(II)-Catalyzed Stereoselective Glycosylation with Glycosyl Trichloroacetimidates

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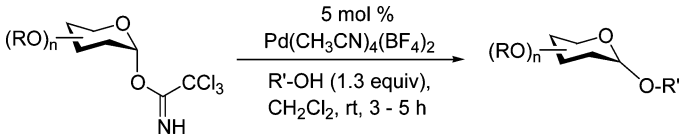
Received November 20, 2007



The development of a new method for stereoselective glycosylation with glycosyl trichloroacetimidate donors employing cationic palladium(II), $Pd(CH_3CN)_4(BF_4)_2$, is described. This process employs $Pd(CH_3CN)_4(BF_4)_2$ as an efficient activator, providing access to a variety of disaccharides and glycopeptides. This reaction is highly stereoselective and proceeds under mild conditions with low catalyst loading. Interestingly, this palladium catalysis directs β-glucosylations in the absence of classical neighboring group participation.

Introduction

Since the first paper on Schmidt's glycosylation method was published in 1980,[1] trichloroacetimidates have been among the most widely used glycosyl donors. Their popularity comes from their relative ease of synthesis by base-catalyzed addition of trichloroacetonitrile to the anomeric hydroxy group.[2] The glycosyl trichloroacetimidates are often formed in high yield with excellent anomeric selectivity. The glycosyl trichloroacetimidates are generally activated with strong and moisture-sensitive Lewis acids such as $BF_3{\cdot}OEt_2$,[1a,3] TMSOTf,[2a,4] TBSOTf,[5] Tf_2O,[6] and ZnBr.[7] These Lewis acids operate under anhydrous and low temperature (up to −78 °C) conditions, especially if glycosyl donors and acceptors are incorporated with acid-labile protecting groups. Additionally, high catalyst loading is often required since these Lewis acids are oxophilic. This has resulted in the continued development of activating reagents and conditions for the activation of trichloroacetimidates. It begins with the use of stoichiometric amounts of AgOTf as a promoter to provide glycosides with excellent yields.[8] Two other improvements utilizing $LiClO_4$ and LiOTf as promoters have been described. The first method requires a large excess of $LiClO_4$.[9] The second method employs a catalytic amount of LiOTf to provide the desired glycoside products as a mixture of α- and β-isomers.[10] Recently, several moisture-stable activating reagents such as I_2/Et_3SiH,[11] $HClO_4$/silica,[12] 4 Å acid-washed molecular sieves,[13] and Amberlyst 15[14] have been shown to successfully activate glycosyl trichloroacetimidates.

We report herein a commercially available cationic Pd(II), $Pd(CH_3CN)_4(BF_4)_2$, catalyzed stereoselective glycosylation with

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(1) (a) Schmidt, R. R.; Michel, J. *Angew. Chem., Int. Ed.* **1980**, *19*, 731−732. For a comprehensive review, see: (b) Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21−123. (c) Schmidt, R. R.; Jung, K.-H. *Adv. Carbohydr. Chem. Biochem.* **2000**, 5−59.

(2) (a) Schmidt, R. R. *Angew. Chem., Int. Ed.* **1986**, *25*, 212−235. (b) Hoos, R.; Huixin, Vasella, J., A.; Weiss, P. *Helv. Chim. Acta* **1996**, *79*, 1757−1784. (c) Patil, V. J. *Tetrahedron Lett.* **1996**, *37*, 1481−1484.

(3) (a) Schmidt, R. R.; Michel, J. *J. Carbohydr. Chem.* **1985**, *4*, 141−169. (b) Zimmermann, P.; Bommer, R.; Bär, T.; Schmidt, R. R. *J. Carbohydr. Chem.* **1988**, *7*, 435−452.

(4) (a) Schmidt, R. R.; Behrendt, M.; Toepfer, A. *Synlett* **1990**, 694−696. (b) Schaubach, R.; Hemberger, J.; Kinzy, W. *Liebigs. Ann. Chem.* **1991**, 607−614. (c) Paulsen, H.; Wilkens, R.; Reck, F.; Brockhausen, I. *Liebigs. Ann. Chem.* **1992**, 1303−1313. (d) Kulkarni, S. S.; Hung, S.-C. *Lett. Org. Chem.* **2005**, *2*, 670−677.

(5) Haase, W. C.; Seeberger, P. H. *Curr. Org. Chem.* **2000**, *4*, 481−511.

(6) Dobarro-Rodriguez, A.; Trumtel, M.; Wessel, H. P. *J. Carbohydr. Chem.* **1992**, *11*, 255−263.

(7) Ubran, F. J.; Moore, B. S.; Breitenbach, R. *Tetrahedron Lett.* **1990**, *31*, 4421−4424.

(8) Douglas, S. P.; Whitfield, D. M.; Krepinsky, J. J. *J. Carbohydr. Chem.* **1993**, *12*, 131−136.

(9) Waldmann, H.; Böhm, Schmid, G., U.; Röttele, H. *Angew. Chem., Int. Ed.* **1994**, *33*, 1944−1996.

(10) Lubineau, A.; Drouillat, B. *J. Carbohydr. Chem.* **1997**, *16*, 1179−1186.

(11) Adinolfi, M.; Barone, G.; Iadonisi, A.; Schiattarella, M. *Synlett* **2002**, 269−270.

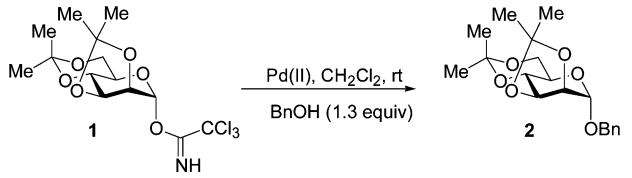
(12) Mukhopadhyway, B.; Maurer, S. V.; Rudolph, N.; van Well, R. M.; Russell, D. A.; Field, R. A. *J. Org. Chem.* **2005**, *70*, 9059−9062.

(13) (a) Adinolfi, M.; Barone, G.; Iadonisi, A.; Schiattarella, M. *Org. Lett.* **2003**, *5*, 987−989. (b) Adinolfi, M.; Barone, G.; Iadonisi, A.; Schiattarella, M. *J. Org. Chem.* **2005**, *70*, 5316−5319.

(14) Tian, Q.; Zhang, S.; Yu, W.; He, M.-B.; Yang, J.-S. *Tetrahedron* **2007**, *63*, 2142−2147.

10.1021/jo702436p CCC: $40.75
Published on Web 01/10/2008

TABLE 1. Efficiency of Pd(II) Catalysts in Glycosylation[a]



entry	Pd(II) source	Pd(II) (mol %)	additive	time (h)	yield[b] (%)	α/β[c]
1	**$Pd(CH_3CN)_4(BF_4)_2$**	**5**	none	**3**	**85**	**α only**
2	$Pd(CH_3CN)_4(BF_4)_2$	3	none	5	70	α only
3	$Pd(CH_3CN)_4(BF_4)_2$	5	DTBP[d]	4	83	α only
4	$Pd(PhCN)_2Cl_2$	5	none	8	<5	

[a] All reactions were carried out in CH_2Cl_2 (0.15 M) for 3−8 h with 1.3 equiv of BnOH. [b] Isolated yield. [c] ^{1}H NMR ratio. [d] DTBP =2,6-di-*tert*-butylpyridine.

glycosyl trichloroacetimidate donors. The cationic palladium(II) species acts a Lewis acid catalyst because it has vacant coordination sites.[15] $Pd(CH_3CN)_4(BF_4)_2$ is air- and moisture-stable and easy to handle; thus, it can be used over a wide range of temperatures and conditions. As compared with neutral Pd(II) species, cationic Pd(II) catalyst exhibits higher activity.[15]

Results and Discussion

The efficacy of $Pd(CH_3CN)_4(BF_4)_2$ as a glycosylation activator was first investigated with 2,3:4,6-bis(di-*O*-isopropylidene)-α-D-mannopyranosyl donor **1** (1 equiv) and freshly distilled benzyl alcohol (1.3 equiv) in the presence of 5 mol % of $Pd(CH_3CN)_4(BF_4)_2$ at 25 °C for 3 h in freshly distilled CH_2Cl_2 (Table 1, entry 1). The desired glycoside **2** was isolated in 85% yield exclusively as α-anomer. The *β*-anomer was not detected by ^{1}H NMR. To determine if HBF_4, which may generate from the cationic palladium catalyst, is the source of catalysis the glycosylation of benzyl alcohol was performed with trichloroacetimidate donor **1** (entry 3) in the presence of 2,6-di-*tert*-butylpyridine (20 mol %) as an acid scavenger. In the event, the formation of the desired glycoside **2** from **1** proceeded in comparable yield to that of entry 1. As a control experiment, a similar glycosylation was attempted with neutral Pd(II) species, $Pd(PhCN)_2Cl_2$ (entry 4); however, less than 5% yield of **2** was detected. These results clearly suggest that $Pd(CH_3CN)_4(BF_4)_2$ is responsible for D-mannopyranosyl trichloroacetimidate **1** activation, and it does so with the formation of **2** in good yield.

With optimized reaction conditions in hand, we set out to define the scope of cationic Pd(II)-catalyzed glycosylation. A number of nucleophilic acceptors, incorporating a variety of protecting groups such as isopropylidene ketals, ester functionality, and *tert*-butyl carbamate group, were examined with glycosyl donor **1** (Table 2, entries 1−4). With the use of primary and secondary hydroxyl of carbohydrate nucleophiles **4** and **5**, disaccharides **10** and **11** were isolated in 93% and 94% yield, respectively (entries 1 and 2). Notably, the efficiency of the reaction is illustrated by the ability to provide **10** and **11** exclusively as α-anomers. When Boc-Ser-OMe (**6**) was probed as potential nucleophile (entry 3), glycopeptide **12** was obtained in 90% yield exclusively as α-anomer. When 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl trichloroacetimidate **3** was employed as glycosyl donor, disaccharides **14**−**16** were isolated

TABLE 2. Glycosylation with D-Mannose Donors[a]

Entry	Donors	Acceptors	Disaccharides Yield[b] (α:β)[c]
1	**1**	**4**	**10** 93% (α)
2	**1**	**5**	**11** 94% (α)
3	**1**	**6**	**12** 90% (α)
4	**1**	**7**	**13** 80% (11:1)
5	**3**	**8**	**14** 75% (α)
6	**3**	**4**	**15** 96% (24:1)
7	**3**	**9**	**16** 72% (α)

[a] All reactions were carried out in CH_2Cl_2 (0.15 M) for 3−5 h with 1.3 equiv of acceptors and 5 mol % of $Pd(CH_3CN)_4(BF_4)_2$. [b] Isolated yield. [c] ^{1}H NMR ratio.

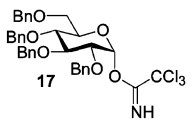
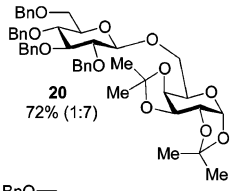
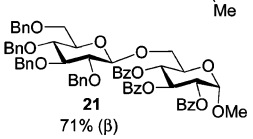
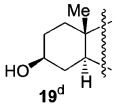
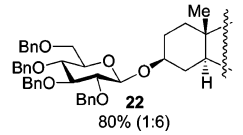
in excellent yields nearly exclusively as α-anomers (Table 1, entries 5−7). Compared to other methods,[16] higher yield and better α-selectivity were observed with the cationic palladium(II)-catalyzed glycosylation with D-mannose donors.

Since the cationic palladium(II)-catalyzed reaction showed excellent α-selectivity with mannose donors at the newly formed glycosidic bond, we examined this chemistry with 2,3,4,6-tetra-*O*-benzyl-D-glycopyranosyl trichloroacetimidate donor **17** (Table 3). Compared to other glycosylation methods,[17] significantly

(15) Mkiami, K.; Hatano, M.; Akiyama, K. *Top. Organomet. Chem.* **2005**, *14*, 270−321 and references therein.

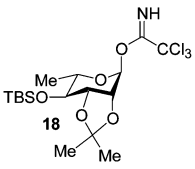
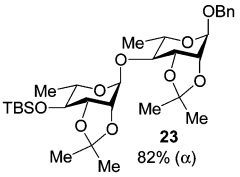
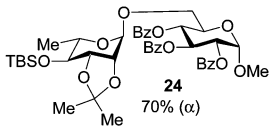
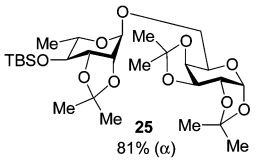
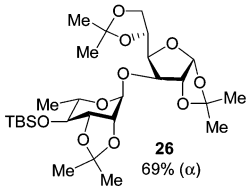
(16) (a) Chretien, F.; Chapleur, Y.; Castro, B.; Gross, B. *J. Chem. Soc., Perkin Trans. 1* **1980**, 381−384. (b) Dasgupta, F.; Garegg, P. *Carbohydr. Res.* **1990**, *202*, 225−238. (c) Suzuki, K.; Maeta, H.; Suzuki, T.; Matsumoto, T. *Tetrahedron Lett.* **1989**, *30*, 6879−6882.

TABLE 3. Glycosylation with D-Glucose Donor[a]

Entry	Donors	Acceptors	Disaccharides Yield[b] (α:β)[c]
1	 **17**	**4**	 **20** 72% (1:7)
2	**17**	**8**	 **21** 71% (β)
3	**17**	 **19**[d]	 **22** 80% (1:6)

[a] All reactions were carried out in CH_2Cl_2 (0.15 M) with 1.3 equiv of acceptors and 5 mol % of $Pd(CH_3CN)_4(BF_4)_2$. [b] Isolated Yield. [c] ^1H NMR ratio. [d] Dihydrocholesterol.

TABLE 4. Glycosylation with L-Rhamnose Donor[a]

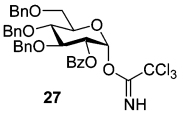
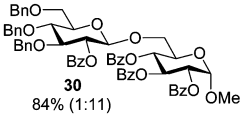
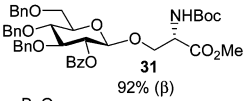
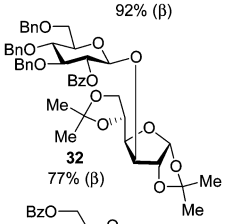
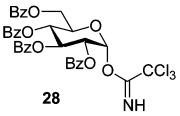
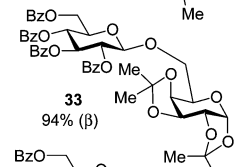
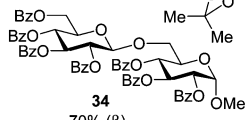
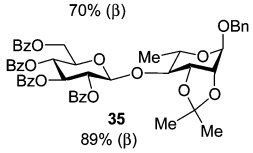
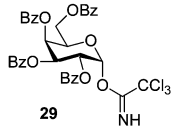
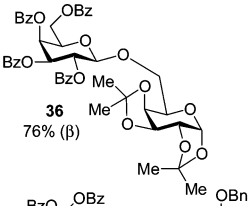
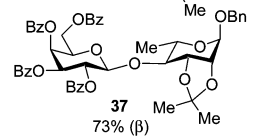
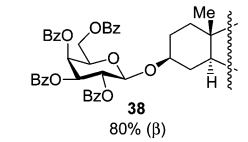
Entry	Donors	Acceptors	Disaccharides Yield[b] (α:β)[c]
1	 **18**	**9**	 **23** 82% (α)
2	**18**	**8**	 **24** 70% (α)
3	**18**	**4**	 **25** 81% (α)
4	**18**	**5**	 **26** 69% (α)

[a] All reactions were carried out in CH_2Cl_2 (0.15 M) with 1.3 equiv of acceptors and 5 mol % of $Pd(CH_3CN)_4(BF_4)_2$. [b] Isolated Yield. [c] ^1H NMR ratio.

better β-selectivity was observed when the glycosylations of nucleophiles **4**, **8**, and **19** were performed with trichloroacetimidate **17**. Disaccharides **20**−**22** were isolated in good yields with good β-selectivity (Table 3). These results were encouraging because they clearly showed that this cationic palladium chemistry could be applied to the β-glucosylations in the absence of neighboring group participation. It has been reported that glycosylation of perbenzylated-D-glycopyranosyl *n*-pentenyl donor with nucleophilic acceptor **4** provided disaccharide **20** in 80% yield with $\alpha/\beta = 1{:}1.4$.[17a] Coupling of perbenzylated-D-glycopyranosyl phosphite donor with glycosyl acceptor **19** has been reported to provide disaccharide **22** in 89% yield with $\alpha/\beta = 1{:}1$.[17b]

On the other hand, use of α-L-rhamnopyranosyl trichloroacetimidate **18** as glycosyl donor provided disaccharides **23**−**26** in good yields exclusively as α-anomers (Table 4). These results are encouraging because they clearly showed that this cationic palladium chemistry could be applied to the ether

TABLE 5. Glycosylation with C(2)-Acyl Glycosyl Donors[a]

Entry	Donors	Acceptors	Disaccharides Yield[b] (α:β)[c]
1	 **27**	**8**	 **30** 84% (1:11)
2	**27**	**6**	 **31** 92% (β)
3	**27**	**5**	 **32** 77% (β)
4	 **28**	**4**	 **33** 94% (β)
5	**28**	**8**	 **34** 70% (β)
6	**28**	**9**	 **35** 89% (β)
7	 **29**	**4**	 **36** 76% (β)
8	**29**	**9**	 **37** 73% (β)
9	**29**	**19**[d]	 **38** 80% (β)

[a] All reactions were carried out in CH_2Cl_2 (0.15 M) with 1.3 equiv of acceptors and 5 mol % of $Pd(CH_3CN)_4(BF_4)_2$. [b] Isolated yield. [c] ^1H NMR ratio. [d] Dihydrocholesterol

(17) (a) Houdier, S.; Vottero, P. J. A. *Carbohydr. Res.* **1992**, *232*, 349−352. (b) Watanabe, Y.; Nakamoto, C.; Yamamoto, T.; Ozaki, S. *Tetrahedron* **1994**, *50*, 6523−6536. (c) Yamanoi, T.; Iwai, Y.; Inazu, T. *J. Carbohydr. Chem.* **1998**, *17*, 819−822.

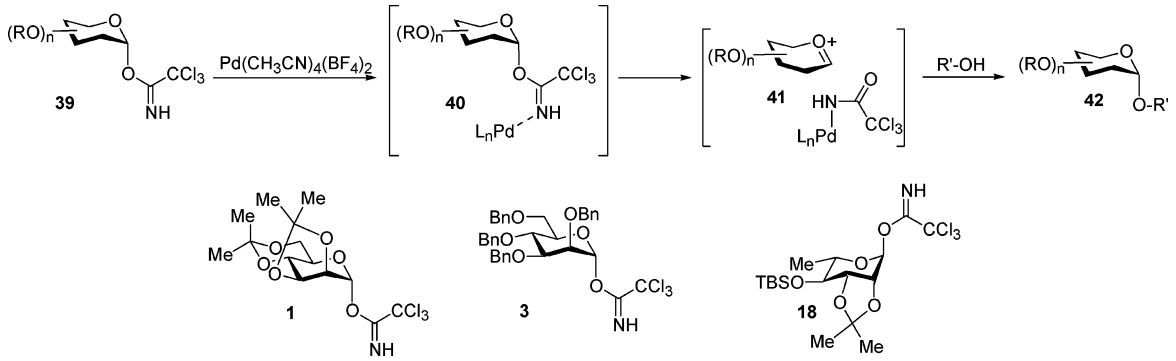


FIGURE 1. Cationic Pd(II)-catalyzed stereoselective formation of α-glycosides.

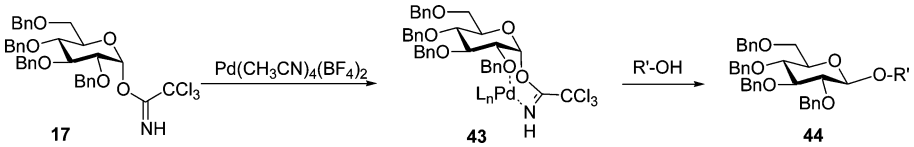


FIGURE 2. Cationic Pd(II)-catalyzed stereoselective formation of β-glycosides.

protecting groups to provide the desired products with excellent α-selectivity.

The remaining glycosyl donors that needed to be tested in the cationic palladium(II)-catalyzed glycosylation reaction were the C(2)-acyl protecting group substrates (Table 5). It is expected that 1,2-trans stereochemical control would be observed at the newly formed glycosidic bond due to the neighboring group participation of the C(2)-acyl functionalities.[1b] Accordingly, coupling of glycosyl donors **27**−**29** with a variety of nucleophiles provided disaccharides **30**−**38** in good yields with excellent β-selectivity.

A possible mechanism for $Pd(CH_3CN)_4(BF_4)_2$-catalyzed stereoselective formation of α-glycosides is outlined in Figure 1. Cationic palladium(II),[18] $Pd(CH_3CN)_4(BF_4)_2$, reversibly coordinates to the imidate nitrogen of **39** to form complex **40** which subsequently undergoes ionization to generate oxocarbenium intermediate **41**. In the case of D-mannose donors **1** and **3** as well as L-rhamnose donor **18**, oxocarbenium ions such as **41** are important reactive intermediates. Due to the steric and anomeric effects that are present in D-mannose and L-rhamnose substrates, axial addition of nucleophiles to **41** should be favored, thus providing the corresponding α-glycoside products **42**.

However, the possible mechanism outlined in Figure 1 is not consistent with D-glucose donor **17**. To rationalize the highly observed β-selectivity, we speculate that the reaction might operate via a seven-membered ring intermediate **43** wherein the C(2)-OBn group of **17** is datively bound to the cationic palladium catalyst (Figure 2). Formation of **43** directs the stereochemistry, leading to the formation of β-glycoside **44**.

Conclusions

In conclusion, we have developed a moisture-tolerant cationic palladium(II), $Pd(CH_3CN)_4(BF_4)_2$, as an efficient activator of α-glycosyl trichloroacetimidate donors. The cationic palladium(II)-catalyzed glycosylation reaction is highly stereoselective and proceeds under mild conditions with low catalyst loading to provide access to a variety of disaccharides and glycopeptides in good yields with excellent stereoselectivity at the anomeric carbon. The advantage of the cationic palladium catalyst is its ability to direct β-glucosylations in the absence of classical neighboring group participation.

Experimental Section

General Glycosylation Procedure with $Pd(CH_3CN)_4(BF_4)_2$: Benzyl 2,3,4,6-Bis(di-*O*-isopropylidene)-α-D-mannopyranoside (2). A 10 mL oven-dried Schlenk flask was charged with α-D-mannopyranosyl trichloroacetimidate **1** (81 mg, 0.20 mmol, 1 equiv), freshly distilled benzyl alcohol (27 μL, 0.26 mmol, 1.3 equiv), and CH_2Cl_2 (1 mL). $Pd(CH_3CN)_4(BF_4)_2$ (4.4 mg, 0.01 mmol, 5 mol %) was then added to the solution. The resulting mixture was stirred at 25 °C for 3 h, diluted with benzene (1 mL), and purified by silica gel flash chromatography (6/1, hexane/ethyl acetate) to give **2** (59.2 mg, 85%) as a white solid: mp = 48−49 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 − 7.26 (m, 5H), 5.05 (s, 1H), 4.77 (dd, J = 6.0, 3.5 Hz, 1H), 4.64 (d, J = 6.0 Hz, 1H), 4.62 (d, J = 11.5 Hz, 1H), 4.47 (d, J = 11.5 Hz, 1H), 4.39 (ddd, J = 7.5, 6.5, 4.5 Hz, 1H), 4.09 (dd, J = 9.0, 6.5 Hz, 1H), 3.98 − 3.94 (m, 2H), 1.44 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.3, 128.5, 128.0, 127.8, 112.6, 109.2, 105.6, 85.1, 80.4, 76.7, 73.1, 69.1, 66.9, 26.9, 25.8, 25.2, 24.5; IR (film, cm^{-1}) ν 3031, 2986, 2937, 1455, 1372, 1210, 1077, 1021, 699; HRMS (ESI) calcd for $C_{19}H_{26}O_6Na$ [M + Na] 373.1622, found 373.1694.

2,3,4,6-Bis(di-*O*-isopropylidene)-α-D-mannopyranosyl-(1→6)-1,2,3,4-bis(di-*O*-isopropylidene)-α-D-galactopyranoside (10). ^{1}H and ^{13}C NMR of disaccharide **10** have been reported:[16a] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.50 (d, J = 5.0 Hz, 1H), 4.99 (s, 1H), 4.75 (dd, J = 6.0, 3.5 Hz, 1H), 4.60 (d, J = 6.0 Hz, 1H), 4.56 (dd, J = 8.0, 2.5 Hz, 1H), 4.34 (ddd, J = 8.0, 6.0, 4.0 Hz, 1H), 4.28 (dd, J = 5.5, 2.5 Hz), 4.17 (dd, J = 8.0, 2.0 Hz, 1H), 4.06 (dd, J = 8.5, 6.0 Hz, 1H), 3.99 (d, J = 9.0, 4.5 Hz, 1H), 3.93 (dd, J = 8.5, 4.0 Hz, 1H), 3.91 (dd, J = 7.0, 2.0 Hz, 1H), 3.70 (dd, J = 10.5, 6.5 Hz, 1H), 3.60 (dd, J = 10.5, 7.0 Hz, 1H), 1.50 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H); ^{1}H NMR matches with the literature report; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 112.6, 109.4, 109.3, 108.6, 106.7, 96.3, 85.0, 80.4, 79.5, 73.0, 70.9, 70.6, 70.5, 66.9, 66.1, 66.0, 26.9, 26.0, 25.9, 25.8, 25.2, 24.9, 24.6, 24.5; ^{13}C NMR matches with the

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literature report; IR (film, cm^{-1}) ν 2987, 2937, 1373, 1256, 1211, 1165, 1069, 1001, 846.

2,3,4,6-Bis(di-*O*-isopropylidene)-α-D-mannopyranosyl-(1→3)-1,2,5,6-bis(di-*O*-isopropylidene)-α-D-glucofuranoside (11). ^1H and ^{13}C NMR of disaccharide **11** have been reported:[16a] ^1H NMR ($CDCl_3$, 500 MHz) δ 5.79 (d, J = 3.0 Hz, 1H), 5.19 (s, 1H), 4.73 (dd, J = 6.0, 3.5 Hz, 1H), 4.58 (d, J = 5.5 Hz, 1H), 4.53 (d, J = 3.5 Hz, 1H), 4.37 (dd, J = 110, 6.0 Hz, 1H), 4.18 (m, 2H), 4.09−3.99 (m, 4H), 3.95−3.92 (m, 2H), 1.45 (s, 3H), 1.42 (s, 6H), 1.37 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H); ^1H NMR matches with the literature report; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 112.7, 111.9, 109.2, 109.1, 107.7, 105.1, 84.9, 83.6, 80.8, 80.7, 79.3, 73.1, 72.3, 67.4, 66.6, 26.9, 26.8, 26.2, 25.8, 25.3, 25.1, 24.5; ^{13}C NMR matches with the literature report; IR (film, cm^{-1}) ν 3365, 3194, 2988, 2938, 1455, 1374, 1213, 1163, 1115, 1078, 1020, 845.

1-*O*-(Boc-L-Ser)- 2,3,4,6-bis(di-*O*-isopropylidene)-α-D-mannopyranoside (12): ^1H NMR ($CDCl_3$, 500 MHz) δ 5.43 (d, J = 9.0 Hz, 1H), 4.91 (s, 1H), 4.75 (dd, J = 6.0, 3.5 Hz, 1H), 4.53 (d, J = 6.0 Hz, 1H), 4.38−4.36 (m, 1H), 4.35 (dd, J = 11.5, 6.5 Hz, 1H), 4.09 (dd, J = 8.5, 6.5 Hz, 1H), 4.01 (dd, J = 8.5, 4.5 Hz, 1H), 3.91−3.87 (m, 2H), 3.80 (dd, J = 10.5, 3.0 Hz, 1H), 3.74 (s, 3H), 1.44 (s, 9H), 1.43 (s, 6H), 1.36 (s, 3H), 1.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.8, 155.4, 112.7, 109.3, 107.2, 84.9, 80.9, 79.4, 72.9, 68.7, 67.0, 53.9, 52.5, 29.7, 28.3, 26.8, 25.8, 25.2, 24.5; IR (film, cm^{-1}) ν 2983, 2936, 1721, 1507, 1370, 1253, 1211, 1163, 1117, 1066, 1028, 827; HRMS (ESI) calcd for $C_{21}H_{35}NO_{10}Na$ [M + Na] 484.2153, found 484.2159.

Methyl 2,3,4,6-bis(di-*O*-isopropylidene)-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-pivaloyl)-α-D-glucopyranoside (13): ^1H NMR ($CDCl_3$, 500 MHz) δ 5.49 (t, J = 9.5 Hz, 1H), 5.00 (s, 1H), 4.83 (d, J = 3.5 Hz, 1H), 4.72 (dd, J = 5.5, 3.5 Hz, 1H), 4.66 (dd, J = 10.5, 4.0 Hz, 1H), 4.49 (t, J = 12.0 Hz, 1H), 4.46 (d, J = 6.0 Hz, 1H), 4.31−4.27 (m, 1H), 4.06−3.95 (m, 4H), 3.83−3.80 (m, 1H), 3.57 (t, J = 9.5 Hz, 1H), 3.32 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H), 1.24 (s, 3H), 1.19 (s, 9H), 1.319 (s, 9H), 1.14 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 177.9, 177.8, 176.9, 112.7, 109.2, 109,1, 96.3, 85.3, 81.1, 79.4, 73.0, 71.4, 71.1, 68.3, 66.7, 63.0, 55.3, 33.9, 33.8, 38.7, 27.2, 27.1, 26.9, 26.6, 25.8, 25.4, 24.6; IR (film, cm^{-1}) ν 2978, 2937, 1734, 1481, 1371, 1281, 1159, 1065, 1037, 977; HRMS (ESI) calcd for $C_{34}H_{56}O_{14}Na$ [M + Na] 711.3568, found 711.3609.

Methyl 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl)-α-D-glucopyranoside (14). ^1H and ^{13}C NMR of disaccharide **14** have been reported:[16b] ^1H NMR ($CDCl_3$, 500 MHz) δ 7.97−7.84 (m, 2H), 7.51−7.14 (m, 33H), 6.09 (t, J = 10.0 Hz, 1H), 5.54 (t, J = 10.0 Hz, 1H), 5.21 (dd, J = 10.0, 3.5 Hz, 1H), 5.15 (d, J = 3.5 Hz, 1H), 4.90 (d, J = 1.0 Hz, 1H), 4.85 (d, J = 10.5 Hz, 1H), 4.70 (d, J = 12.5 Hz, 1H), 4.66 (d, J = 12.5 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.50−4.42 (m, 3H), 4.37 (d, J = 12.0 Hz, 1H), 4.15−4.11 (m, 1H), 3.93 (t, J = 9.0 Hz, 1H), 3.88−3.83 (m, 3H), 3.68−3.67 (m, 1H), 3.64−3.58 (m, 3H), 3.53−3.50 (m, 1H), 3.37 (s, 3H); ^1H NMR matches with the literature report; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.8, 165.1, 138.7, 138.6, 138.4, 138.3, 133.3, 133.2, 133.1, 129.9, 129.6, 129.3, 129.1, 128.6, 128.4, 128.31, 128.3, 128.2, 127.9, 127.8, 127.7, 127.52, 127.5, 127.4, 98.2, 96.9, 79.8, 74.9, 74.8, 74.7, 73.2, 72.5, 72.1, 71.8, 70.5, 69.8, 68.9, 68.1, 66.1, 55.5; ^{13}C NMR matches with the literature report; IR (film, cm^{-1}) ν 3063, 3031, 2933, 2871, 1730, 1453, 1280, 1265, 1106, 1069, 1027, 916, 825.

2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl-(1→6)-1,2,3,4-bis(di-*O*-isopropylidene)-α-D-galactopyranoside (15). The synthesis of disaccharide **15** has been reported:[19] ^1H NMR (C_6D_6, 500 MHz) δ 7.46−7.45 (m, 2H), 7.40−7.36 (m, 4H), 7.31−7.29 (m, 2H), 725−7.13 (m, 12H), 5.58 (d, J = 5.0 Hz, 1H), 5.28 (s, 1H), 5.03 (d, J = 11.5 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.68−4.64 (m, 3H), 4.58 (dd, J = 8.0, 2.0 Hz, 1H), 4.52−4.45 (m, 3H), 4.39 (dd, J = 14.5, 4.5 Hz, 1H), 4.32 (t, J = 6.0 Hz, 1H), 4.26−4.21 (m, 3H), 4.17 (ddd, J = 10.5, 6.5, 3.0 Hz, 1H), 4.12 (d, J = 8.0 Hz, 1H), 4.00−3.96 (m, 2H), 3.89 (dd, J = 11.0, 5.0 Hz, 1H), 3.78 (d, J = 11.0 Hz), 1.51 (s, 3H), 1.50 (s, 3H), 1.23 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 139.4, 139.2, 139.1, 138.9, 128.3, 128.2, 128.1, 127.72, 127.7, 127.4, 127.3, 127.23, 127.2, 109.2, 108.2, 97.8, 96.6, 80.6. 75.7, 75.3, 74.8, 73.3, 72.9, 72.7, 71.9, 71.3, 71.1, 70.7, 69.6, 66.1, 65.9, 26.0, 24.6, 24.3; IR (film, cm^{-1}) ν 2987, 2916, 1496, 1454, 1381, 1371, 1255, 1211, 1167, 1100, 1070, 1027, 1002; HRMS (ESI) calcd for $C_{46}H_{54}O_{11}Na$ [M + Na] 805.3558, found 805.3527.

Benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→4)-2,3,-di-*O*-isopropylidene-α-L-rhamnopyranoside (16): ^1H NMR (C_6D_6, 500 MHz) δ 7.36−7.15 (m, 25H), 7.40−7.36 (m, 4H), 4.96 (s, 1H), 4.92 (s, 1H), 4.87 (d, J = 11.0 Hz, 1H), 4.75 (d, J = 12.5 Hz, 1H), 4.72 (d, J = 12.5 Hz, 1H), 4.68 (d, J = 12.5 Hz, 1H), 4.66−4.59 (m, 3H), 4.52 (d, J = 10.5 Hz, 1H), 4.47 (t, J = 11.5 Hz, 2H), 4.19 (t, J = 10.0 Hz, 1H), 4.08 (d, J = 5.5 Hz, 1H), 4.01−3.97 (m, 2H), 3.87 (dd, J = 10.5, 3.0 Hz, 1H), 3.83 (dd, J = 9.5, 3.0 Hz, 1H), 3.72−3.71 (m, 1H), 3.65 (dd, J = 11.0, 1.5 Hz, 1H), 3.59 (dq, J = 8.5, 6.5 Hz, 1H), 3.32 (dd, J = 10.0, 7.5 Hz, 1H), 1.44 (s, 3H), 1.23 (s, 3H), 1.02 (d, J = 6.0 Hz, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 138.8, 138.6, 138.2, 128.5, 128.3, 128.25, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 109.0, 98.9, 96.1, 80.2, 80.1, 76.0, 75.2, 74.7, 74.2, 73.4, 72.6, 72.3, 71.8. 69.1, 68.7, 65.0, 28.1, 26.3, 17.3; IR (film, cm^{-1}) ν 3029, 2984, 2934, 1496, 1454, 1380, 1242, 1219, 1139, 1093, 1051, 1027, 994, 861; HRMS (ESI) calcd for $C_{50}H_{56}O_{10}Na$ [M + Na] 839.3771, found 839.3762.

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→6)-1,2,3,4-bis(di-*O*-isopropylidene)-α-D-galactopyranoside (20). ^1H and ^{13}C NMR of disaccharide **20** have been reported:[20] R_f = 0.36 (hexane/ethyl acetate, 4/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.44−7.14 (m, 20H), 5.58 (d, J = 5.0 Hz, 1H), 5.07 (d, J = 11 Hz, 1H), 4.97 (d, J = 11 Hz, 1H), 4.82 (d, J = 11 Hz, 1H), 4.79 (d, J = 11 Hz, 1H), 4.73 (d, J = 11 Hz, 1H), 4.65−4.58 (m, 2H), 4.55 (s, 1H), 4.51 (d, J = 11 Hz, 1H), 4.47 (d, J = 7.5 Hz, 1H), 4.33−4.31 (m, 1H), 4.25 (d, J = 8 Hz, 1H), 4.17 (dd, J = 10.5, 3.5 Hz, 1H), 4.1 (m, 1H), 3.83−3.68 (m, 3H), 3.67−3.58 (m, 2H), 3.49−3.45 (m, 2H), 1.51 (s, 3H), 1.46 (s, 3H), 1.32 (2s, 6H); ^1H NMR matches with the literature report; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.7, 138.2, 128.7, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.55, 127.49, 109.4, 108.6, 104.4, 96.4, 84.6, 81.6, 77.7, 75.7, 75.0, 74.8, 74.4, 73.5, 71.5, 70.8, 70.5, 69.7, 68.8, 67.4, 26.1, 26.0, 25.1, 24.5; ^{13}C NMR matches with the literature report; $J(^{13}CH)$ = 156 Hz (104.4 ppm); 179 Hz (96.4 ppm); IR (film, cm^{-1}) ν 2902, 1454, 1381, 1255, 1211.

Methyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (21). ^1H and ^{13}C NMR of disaccharide **20** have been reported:[21] R_f = 0.18 (hexane/ethyl acetate, 6/1); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, J = 7.5 Hz, 2H), 7.92 (d, J = 7.0 Hz, 2H), 7.84 (d, J = 7.0 Hz, 2H), 7.51−7.13 (m, 29H), 6.16 (t, J = 10 Hz, 1H), 5.48 (t, J = 10 Hz, 1H), 5.25 (dd, J = 10, 3.5 Hz, 1H), 5.20 (d, J = 2.5 Hz, 1H), 5.05 (d, J = 10.5 Hz, 1H), 4.90 (d, J = 11 Hz, 1H), 4.82−4.74 (m, 2H), 4.68 (d, J = 10 Hz, 1H), 4.53−4.35 (m, 5H), 4.12 (d, J = 10 Hz, 1H), 3.80 (dd, J = 10.5, 7 Hz, 1H), 3.64−3.57 (m, 4H), 3.49−3.40 (m, 2H), 3.37 (s, 3H); ^1H NMR matches with the literature report; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.84, 165.80, 165.5, 138.6, 138.5, 138.10, 138.07, 133.42, 133.35, 133.08, 130.0, 129.9, 129.7, 129.2, 129.1, 128.9, 128.4, 128.35, 128.26, 128.2, 127.93, 127.87, 127.75, 127.67, 127.57, 127.5, 104.0, 96.8, 84.5, 82.3, 81.7, 77.7,

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75.7, 75.0, 74.9, 74.8, 73.4, 72.1, 70.5, 69.9, 69.0, 68.8, 68.6, 55.5; ^{13}C NMR matches with the literature report; $J(^{13}CH) = 155$ Hz (104.0 ppm); 173 Hz (96.8 ppm); IR (film, cm^{-1}) ν 2916, 1730.

1-*O*-Dihydrocholesterolyl-2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (22β). ^{1}H and ^{13}C NMR of disaccharide **20** have been reported:[22] $R_f = 0.44$ (hexane/ethyl acetate, 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35−7.15 (m, 20H), 4.96 (d, $J = 11$ Hz, 1H), 4.91 (d, $J = 11$ Hz, 1H), 4.81 (d, $J = 11$ Hz, 1H), 4.77 (d, $J = 11$ Hz, 1H), 4.71 (d, $J = 11$ Hz, 1H), 4.61−4.51 (m, 3H), 4.51 (d, $J = 8$ Hz, 1H), 3.74 (d, $J = 10.5$ Hz, 1H), 3.65−3.60 (m, 3H), 3.52 (t, $J = 9.0$ Hz, 1H), 3.46−3.40 (m, 2H), 1.98−0.58 (m, 47H); ^{1}H NMR matches with the literature report; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.7, 138.6, 138.3, 138.2, 128.4, 128.33, 128.26, 128.0, 127.9, 127.73, 127.67, 127.62, 127.55, 127.52, 101.9, 84.9, 82.4, 79.1, 78.1, 75.7, 75.0, 74.8, 73.4, 69.3, 56.5, 56.3, 54.4, 44.8, 42.6, 40.1, 39.5, 37.1, 36.2, 35.8, 35.6, 35.5, 34.8, 32.1, 29.7, 28.8, 28.3, 28.0, 24.2, 23.8, 22.8, 22.6, 21.2, 18.7, 12.3, 12.1; ^{13}C NMR matches with the literature report; IR (film, cm^{-1}) ν 2931, 2866, 1453, 1360.

1-*O*-Dihydrocholesterolyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (22α): $R_f = 0.44$ (hexane/ethyl acetate, 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34−7.11 (m, 20H), 4.98 (d, $J = 11$ Hz, 1H), 4.91 (d, $J = 3$ Hz, 1H), 4.81 (d, $J = 11$ Hz, 1H), 4.79 (d, $J = 11$ Hz, 1H), 4.74 (d, $J = 12$ Hz, 1H), 4.65 (d, $J = 12$ Hz, 1H), 4.44 (d, $J = 11.5$ Hz, 2H), 3.97 (t, $J = 9$ Hz, 1H), 3.86 (t, $J = 9.5$ Hz, 1H), 3.71 (dd, $J = 10$, 3 Hz, 1H), 3.68−3.51 (m, 4H), 1.96−0.56 (m, 47H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.0, 138.3, 128.4, 128.34, 128.32, 128.1, 127.9, 127.83, 127.80, 127.65, 127.61, 127.5, 94.7, 82.1, 80.0, 77.9, 76.3, 75.6, 75.1, 73.4, 73.0, 70.0, 68.7, 56.5, 56.3, 54.4, 45.1, 42.6, 40.0, 39.5, 36.9, 36.2, 35.84, 35.78, 35.7, 35.5, 32.1, 28.7, 28.2, 28.0, 27.4, 24.2, 23.8, 22.8, 22.5, 21.2, 18.7, 12.3, 12.1; IR (film, cm^{-1}) ν 2928, 2865, 1453.

Benzyl 4-*O*-*tert*-butyldimethylsilyl-2,3,-di-*O*-isopropylidene-α-L-rhamnopyranosyl-(1 → 4)-2,3-di-*O*-isoproylidene-α-L-rhamnopyranoside (23): $R_f = 0.42$ (hexane/ethyl acetate, 6/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34−7.29 (m, 5H), 5.54 (s, 1H), 5.04 (s, 1H), 4.68 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 11.5$ Hz, 1H, Bn), 4.21 (t, $J = 6.5$ Hz, 1H), 4.12 (d, $J = 5.5$ Hz, 1H), 4.10 (d, $J = 5.5$ Hz, 1H), 3.91 (t, $J = 6.0$ Hz, 1H), 3.74−3.68 (m, 1H), 3.59−3.53 (m, 2H), 3.32 (dd, $J = 9.5$, 7.5 Hz, 1H), 1.52 (s, 3H), 1.50 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.26 (d, $J = 6$ Hz, 3H), 1.19 (d, $J = 6.5$ Hz, 3H), 0.88 (s, 9H,), 0.12 (s, 3H), 0.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.1, 128.5, 128.2, 127.9, 109.4, 108.7, 96.2, 95.9, 78.9, 78.6, 76.7, 76.5, 76.1, 75.7, 69.1, 66.4, 64.2, 28.1, 27.9, 26.4, 25.9, 17.9, 17.5, −4.0, −4.8; IR (film, cm^{-1}) ν 2934, 1381, 1245, 1221, 1086; HRMS (ESI) calcd for $C_{31}H_{50}O_9SiNa$ (M + Na) 617.3116, found 617.3097.

Methyl 4-*O*-*tert*-butyldimethylsilyl-2,3,-di-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (24): $R_f = 0.49$ (hexane/ethyl acetate, 2/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.97−7.92 (m, 4H), 7.85 (d, $J = 8$ Hz, 2H), 7.51−7.34 (m, 7H), 7.27 (t, $J = 8$ Hz, 2H), 6.13 (t, $J = 10$ Hz, 1H), 5.56 (t, $J = 10$ Hz, 1H), 5.24 (dd, $J = 10$, 3.5 Hz, 1H), 5.21 (d, $J = 3.5$ Hz, 1H), 4.91 (s, 1H), 4.22−4.18 (m, 1H), 4.07 (d, $J = 6$ Hz, 1H), 3.86−3.82 (m, 2H), 3.62 (dd, $J = 11.5$, 5.5 Hz, 1H), 3.52 (dd, $J = 10$, 6.5 Hz, 1H), 3.46 (s, 3H), 3.25 (dd, $J = 9.5$, 7.5 Hz, 1H), 1.47 (s, 3H), 1.29 (s, 3H), 1.10 (d, $J = 6$ Hz, 3H), 0.87 (s, 9H), 0.11 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.82, 165.79, 165.3, 133.5, 133.4, 133.3, 133.0, 129.9, 129.8, 129.7, 128.41, 128.39, 128.3, 108.8, 97.8, 97.0, 78.9, 75.86, 75.80, 72.1, 70.5, 69.7, 68.7, 55.6, 29.7, 28.1, 26.4, 25.9, 17.5, −4.0, −4.9; IR (film, cm^{-1}) ν 2930, 1732, 1280, 1265; HRMS (ESI) calcd for $C_{43}H_{54}O_{13}SiNa$ (M + Na) 829.3226, found 829.3221.

4-O-*tert*-Butyldimethylsilyl-2,3,-di-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→6)-1,2,3,4-bis(di-*O*-isopropylidene)-α-D-galactopyranoside (25): $R_f = 0.37$ (hexane/ethyl acetate, 6/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.51 (d, $J = 5$ Hz, 1H), 4.96 (s, 1H), 4.58 (dd, $J = 8$, 2.5 Hz, 1H), 4.29 (dd, $J = 5$, 2.5 Hz, 1H), 4.24 (dd, $J = 7.5$, 1.5 Hz, 1H), 4.13 (d, $J = 5.5$ Hz, 1H), 3.95 (t, $J = 6.5$ Hz, 1H), 3.84 (dd, $J = 10$, 6 Hz, 1H), 3.63−3.56 (m, 2H), 3.29 (dd, $J = 9.5$, 7 Hz, 1H), 1.52 (s, 3H), 1.49 (s, 3H), 1.43 (s, 3H), 1.31 (s, 9H), 1.19 (d, $J = 6.5$ Hz, 3H), 0.86 (s, 9H), 0.12 (s, 3H), 0.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 109.2, 108.9, 108.5, 97.0, 96.3, 79.1, 76.0, 75.9, 71.0, 70.6, 66.5, 65.9, 65.3, 28.1, 26.4, 26.1, 26.0, 25.9, 24.9, 24.3, 17.6, −4.0, −4.9; IR (film, cm^{-1}) ν 2934, 1382; HRMS (ESI) calcd for $C_{27}H_{48}O_{10}SiNa$ (M + Na) 583.2909, found 583.2927.

4-*O*-*tert*-Butyldimethylsilyl-2,3,-di-*O*-isopropylidene-α-L-rhamnopyranosyl-(1→3)-1,2,5,6-bis(di-*O*-isopropylidene)-α-D-glucofuranoside (26): $R_f = 0.34$ (hexane/ethyl acetate, 6/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.86 (d, $J = 3.5$ Hz, 1H), 5.08 (s, 1H), 4.53 (d, $J = 3.5$ Hz, 1H), 4.40 (d, $J = 3.5$ Hz, 1H), 4.26−4.23 (m, 1H), 4.11 (dd, $J = 8.5$, 6.5 Hz, 1H), 4.08 (dd, $J = 8.5$, 3 Hz, 1H), 4.05 (d, $J = 5.5$ Hz, 1H), 3.93−3.87 (m, 2H), 3.84 (dd, $J = 10$, 6 Hz, 1H), 3.30 (dd, $J = 10$, 7 Hz, 1H), 1.50 (s, 3H), 1.49 (s, 3H), 1.38 (s, 3H), 1.32 (s, 3H), 1.29 (s, 6H), 1.16 (d, $J = 6.5$ Hz, 3H), 0.85 (s, 9H), 0.11 (s, 3H), 0.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 112.0, 109.1, 109.0, 105.3, 94.6, 81.7, 81.0, 79.2, 76.1, 76.0, 75.5, 71.7, 68.0, 66.4, 28.1, 26.74, 26.69, 26.4, 26.1, 25.8, 25.1, 17.4, −3.9, −5.0; IR (film, cm^{-1}) ν 2934, 1381, 1372, 1078; HRMS (ESI) calcd for $C_{27}H_{48}O_{10}SiNa$ (M + Na) 583.2909, found 583.2918.

Methyl 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (30). The synthesis of disaccharide **30** has been reported:[23] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.05−7.78 (m, 8H), 7.56−7.18 (m, 27H), 6.05 (t, $J = 10.0$ Hz, 1H), 5.30 (t, $J = 9.0$ Hz, 1H), 5.27 (d, $J = 7.0$ Hz, 1H), 5.06 (dd, $J = 10.0$, 3.5 Hz, 1H), 4.85 (d, $J = 3.5$ Hz, 1H), 4.80 (d, $J = 11.0$ Hz, 1H), 4.73 (d, $J = 11.0$ Hz, 1H), 4.67 (d, $J = 11.0$ Hz, 1H), 4.61−4.52 (m, 3H), 4.47 (d, $J = 12.0$ Hz, 1H), 4.17 (ddd, $J = 10.0$, 8.5, 1.5 Hz, 1H), 4.07 (dd, $J = 11.0$, 1.5 Hz, 1H), 3.84 (d, $J = 9.0$ Hz, 1H), 3.77 (t, $J = 9.0$ Hz, 1H), 3.73−3.68 (m, 2H), 3.64 (dd, $J = 11.0$, 8.0 Hz, 1H), 3.52 (dd, $J = 9.5$, 5.5, 3.5 Hz, 1H), 3.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.71, 165.7, 165.5, 165.3, 133.4, 133.3, 133.1, 133.0, 129.9, 129.8, 129.6, 128.4, 128.3, 128.25, 128.2, 127.9, 127.8, 127.7, 127.63, 127.6, 101.7, 96.3, 82.7, 77.9, 77.3, 77.0, 76.8, 75.3, 75.1, 75.0, 73.7, 73.5, 72.0, 70.5, 69.7, 68.9, 68.7, 68.4, 54.9; IR (film, cm^{-1}) ν 2936, 1728, 1452, 1094, 1069, 1027, 735.

1-*O*-(Boc-L-Ser)-2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (31): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.02 (d, $J = 7.5$ Hz, 2H), 7.58−7.11 (m, 18H), 5.28 (d, $J = 8.0$ Hz, 1H), 5.22 (t, $J = 8.5$ Hz, 1H), 4.80 (d, $J = 10.5$ Hz, 1H), 4.73 (d, $J = 11.5$ Hz, 1H), 4.65 (d, $J = 11.0$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 1H), 4.56 (dd, $J = 10.5$, 4.5 Hz, 1H), 4.52 (d, $J = 8.0$ Hz, 1H), 4.34 (dd, $J = 8.0$, 3.5 Hz, 1H), 4.24 (d, $J = 10.0$ Hz, 1H), 3.81−3.77 (m, 3H), 3.74 (d, $J = 3.0$ Hz, 2H), 3.03 (s, 3H), 3.36 (bs, 1H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 165.2, 155.4, 137.9, 137.8, 137.7, 133.2, 129.8, 128.4, 128.3, 128.0, 127.9, 127.8, 127.72, 127.7, 101.2, 82.5, 77.7, 75.3, 75.1, 74.9, 73.6, 73.4, 68.9, 68.5, 53.9, 52.5, 28.3; IR (film, cm^{-1}) ν 3437, 3353, 3296, 2951, 2870, 1723, 1601, 1497, 1453, 1365, 1268, 1161, 1094, 1070, 826, 737, 712, 699; HRMS (ESI) calcd for $C_{43}H_{49}NO_{11}Na$ [M + Na] 778.3203, found 778.3224.

2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl-(1→3)-1,2,5,6-bis(di-*O*-isopropylidene)-α-D-glucofuranoside (32): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.97 (d, $J = 7.5$ Hz, 2H), 7.58−7.11 (m, 18H), 5.35 (d, $J = 4.0$ Hz, 1H), 5.19 (t, $J = 8.5$ Hz, 1H), 4.80 (d, $J = 11.0$ Hz, 1H), 4.73 (d, $J = 11.0$ Hz, 1H), 4.65−4.54 (m, 5H), 4.36 (dd, $J = 11.0$, 6.0 Hz, 1H), 4.26−4.22 (m, 3H), 4.02 (dd, $J = 9.0$, 7.0 Hz, 1H), 3.93 (dd, $J = 9.0$, 6.0 Hz, 1H), 3.81−3.75 (m, 2H), 3.73 (d, $J = 3.0$ Hz, 2H), 3.54−3.53 (m, 1H), 1.39 (s, 3H), 1.36 (s, 3H), 1.25 (s, 3H), 1.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.8, 138.0, 137.8, 137.7, 133.4, 129.6, 128.53, 128.5,

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128.4, 128.3, 128.1, 127.97, 127.9, 127.8, 127.72, 127.7, 111.8, 108.5, 104.9, 99.7, 82.7, 82.3, 80.7, 80.4, 77.8, 75.7, 75.1, 74.8, 73.7, 73.6, 73.2, 68.5, 65.9; IR (film, cm^{-1}) ν 2987, 2935, 1723, 1600, 1453, 1372, 1266, 1071, 1026, 826, 712, 698; HRMS (ESI) calcd for $C_{46}H_{52}O_{12}Na$ [M + Na] 819.3351, found 819.3347.

2-3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-1,2,5,6-bis(di-*O*-isopropylidene)-α-D-glucopyranoside (33). The synthesis of disaccharide **33** has been reported:[24] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.01 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.53−7.24 (m, 12H), 5.88 (t, J = 9.5 Hz, 1H), 5.65 (t, J = 9.5 Hz, 1H), 5.51 (dd, J = 9.5, 8.0 Hz, 1H), 5.40 (d, J = 5.0 Hz, 1H), 5.01 (d, J = 8.0 Hz, 1H), 4.62 (dd, J = 12.0, 3.0 Hz), 4.46 (dd, J = 12.0, 5.5 Hz, 1H), 4.40 (dd, J = 8.0, 2.5 Hz, 1H), 4.18 (dd, J = 5.0, 2.5 Hz, 1H), 4.15 (ddd, J = 8.5, 5.0, 3.0 Hz, 1H), 4.07 (dd, J = 8.0, 1.5 Hz, 1H), 4.00 (dd, J = 10.5, 3.5 Hz, 1H), 3.88−3.81 (m, 2H), 1.35 (s, 3H), 1.22, (s, 3H), 1.18 (s, 3H), 1.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 165.8, 165.2, 165.1, 133.4, 133.1, 133.0, 130.0, 129.8, 129.7, 129.4, 128.9, 128.8, 128.7, 128.4, 128.3, 128.24, 128.2, 109.3, 108.4, 101.2, 96.2, 73.0, 72.2, 71.8, 70.9, 70.5, 70.4, 69.8, 68.3, 67.5, 63.2, 25.9, 25.7, 24.8, 24.2; IR (film, cm^{-1}) ν 1730, 1601, 1452, 1374, 1266, 1094, 1069, 1026, 825, 709.

Methyl 2-3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (34). The synthesis of disaccharide **34** has been reported:[25] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (dd, J = 8.0, 7.0 Hz, 4H), 7.90 (d, J = 7.0 Hz, 2H), 7.87 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 7.5 Hz, 2H), 7.80 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.53−7.20 (m, 16H), 6.04 (t, J = 10.0 Hz, 1H), 5.89 (t, J = 10.0 Hz, 1H), 5.63 (t, J = 10.0 Hz, 1H), 5.54 (d, J = 9.5, 7.5 Hz, 1H), 5.29 (t, J = 9.5 Hz, 1H), 5.06 (dd, J = 10.0, 2.5 Hz, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.91 (d, J = 4.0 Hz, 1H), 4.58 (dd, J = 12.5, 3.0 Hz, 1H), 4.42 (dd, J = 12.0, 5.0 Hz, 1H), 4.19 (t, J = 8.0 Hz, 1H), 4.12 (dd, J = 9.5, 4.0 Hz, 1H), 4.08 (d, J = 11.0 Hz, 1H), 3.76 (dd, J = 11.5, 7.5 Hz, 1H), 3.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 165.8, 165.6, 165.4, 165.2, 133.4, 133.3, 133.2, 133.1, 133.0, 129.8, 129.7, 129.6, 129.3, 129.2, 129.0, 128.7, 128.4, 128.31, 128.3, 128.2, 101.7, 96.4, 72.8, 72.3, 71.9, 71.8, 70.3, 69.6, 68.9, 68.7, 63.0, 55.0; IR (film, cm^{-1}) ν 2929, 1729, 1601, 1451, 1315, 1267, 1108, 1094, 1069, 1026, 911, 708.

Benzyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (35): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.07−7.81 (m, 7H), 7.53−7.17 (m, 18H), 5.89 (t, J = 10.0 Hz, 1H), 5.62 (t, J = 10.0 Hz, 1H), 5.46 (dd, J = 10.0, 8.0 Hz, 1H), 5.31 (d, J = 8.0 Hz, 1H), 4.96 (s, 1H), 4.65 (dd, J = 5.5, 2.5 Hz, 1H), 4.60 (d, J = 12.0 Hz, 1H), 4.46 (d, J = 5.5 Hz, 1H), 4.41 (d, J = 11.5 Hz, 1H), 4.11 (ddd, J = 9.5, 5.5, 3.5 Hz, 1H), 4.01−3.96 (m, 2H), 3.63 (dq, J = 9.5, 6.0 Hz, 1H), 3.56 (dd, J = 10.0, 6.5 Hz, 1H), 1.45 (s, 3H), 1.26 (d, J = 6.0 Hz, 3H), 1.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 165.8, 165.3, 136.9, 133.6, 133.2, 133.1, 130.0, 129.9, 129.8, 129.76, 129.7, 129.6, 129.5, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.9, 109.2, 100.4, 95.9, 80.7, 78.0, 76.0, 73.1, 72.3, 72.1, 70.0, 69.1, 64.0, 63.2, 29.7, 27.9, 26.2, 17.5; IR (film, cm^{-1}) ν 2983, 2933, 1732, 1601, 1452, 1380, 1266, 1177, 1106, 1092, 1069, 1026, 733, 709, 686; HRMS (ESI) calcd for $C_{50}H_{48}O_{14}Na$ [M + Na] 895.2936, found 895.2929.

2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-1,2,5,6-bis(di-*O*-isopropylidene)-α-D-galactopyranoside (36): R_f = 0.38 (benzene/ethyl acetate, 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.07 (d, J = 7.5 Hz, 2H), 8.01 (d, J = 7.5 Hz, 2H), 7.96 (d, J = 7.5, 2H), 7.76 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.46 (m, 3H), 7.41 (t, J = 8 Hz, 3H) 7.34 (t, J = 7.5 Hz, 2H), 7.22 (m, 3H), 5.97 (d, J = 2.5 Hz, 1H), 5.79 (t, J = 10 Hz, 1H), 5.59 (dd, J = 10.0, 3.0 Hz, 1H), 5.40 (d, J = 4 Hz, 1H), 5.0 (d, J = 8 Hz, 1H), 4.65 (dd, J = 11.0, 6.5 Hz, 1H), 4.40 (m, 2H), 4.32 (t, J = 6.6 Hz,1H), 4.19 (d, J = 2.5 Hz, 1H), (m, 1H), 4.04 (m, 1H), 3.89 (m, 2H), 1.37 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H), 1.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.0, 165.6, 165.5, 165.3, 133.5, 133.2, 133.0, 129.9, 129.8, 128.6, 128.4, 128.3, 128.2, 109.3, 108.4, 101.7, 96.2, 71.8, 71.3, 71.0, 70.5, 70.3, 69.7, 68.4, 68.2, 67.4, 62.0, 25.9, 25.7, 24.8, 24.2; IR (film, cm^{-1}) ν 3065, 2985, 2935, 1727, 1605, 1453, 1381, 1267, 1103, 1069; HRMS (ESI) calcd for $C_{46}H_{46}O_{15}Na$ [M + Na] 861.2734, found 895.2766.

Benzyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-,2,3-*O*-isopropylidene)-α-L-rhamnopyranoside (37): R_f = 0.29 (benzene/ethyl acetate, 25/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.06 (d, J = 7 Hz, 2H), 8.00 (dd, J = 7, 4 Hz, 4H), 7.78 (d, J=7 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.54(t, J = 7.5 Hz, 1H), 7.48 (t, = 7.5 Hz, 3H), 7.41 (t, J = 7.5 Hz, 3H), 7.35 (m, 9H), 7.31 (t, J = 6 Hz, 2H), 7.26 (m, 3H), 5.96 (d, J = 2.5 Hz, 1H), 5.71 (t, J = 10.5 Hz, 1H), 5.59 (dd, J = 10.5, 3.5 Hz, 1H), 5.23 (d, J = 8 Hz, 1H), 4.98 (s, 1H), 4.62 (m, 2H), 4.42 (m, 2H), 4.29 (t, J = 6 Hz, 1H), 4.01 (s, 1H), 3.99 (m, 1H), 3.70 (m, 1H), 3.58 (m, 1H), 1.46 (s, 3H), 1.34 (d, J = 6.5 Hz, 3H), 1.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.6, 133.5, 133.3, 133.2, 133.1, 129.9, 128.6, 128.5, 128.4, 128.3, 128.0, 101.2, 96.0, 81.5, 78.0, 76.0, 71.9, 71.4, 70.0, 69.1, 68.3, 64.1, 62.2, 27.9, 26.1, 17.6; IR (film, cm^{-1}) ν 3063, 3033, 2964, 2935, 1730, 1602, 1450, 1261, 1095, 1068; HRMS (ESI) calcd for $C_{50}H_{48}O_{14}Na$ [M + Na] 895.2936, found 895.2929.

1-*O*-D-Hydrocholesterolyl-2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside (38): R_f = 0.36 (benzene/ethyl acetate, 40/1); ^{1}HNMR ($CDCl_3$, 500 MHz) δ 8.09(d, J = 7.5 Hz, 2H), 8.01(d, J = 7.5 Hz, 2H), 7.94(d, J = 7.0 Hz, 2H), 7.77(d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.49 (m, 3H), 7.42 (t, J = 10 Hz, 3H), 7.36 (m, 3H), 7.22 (m, 2H), 5.96 (d, J = 2.5 Hz, 1H), 5.74 (t, J = 10.5 Hz, 1H), 5.56 (dd, J = 10.5, 3.5 Hz,1H), 4.86 (d, J = 8 Hz, 1H), 4.66 (dd, J = 11.5, 7 Hz, 1H), 4.41 (dd, J = 11, 6.5 Hz, 1H), 4.30 (t, J = 6.5 Hz, 1H), 3.61(m, 1H), 2.0−0.5(m, 47H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.0, 165.7, 165.3, 165.2, 130.1, 129.8, 129.7, 128.8, 128.6, 128.4, 128.3, 128.2, 100.6, 80.5, 71.9, 71.2, 70.0, 68.2, 62.1, 56.4, 56.3, 54.3, 44.7, 42.6, 40.0, 39.5, 36.9, 36.2, 35.8, 35.5, 35.4, 34.7, 32.0, 29.4, 28.6, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.2, 18.7; IR (film, cm^{-1}) ν 3067, 2935, 2863, 1730, 1602, 1450, 1266, 1106, 1068, 1027; HRMS (ESI) calcd for $C_{61}H_{74}O_{10}Na$ [M + Na] 989.5174, found 989.5133.

Acknowledgment. We thank Montana State University and NSF EPSCoR for financial support. We also thank Dr. Gregory J. Mercer for obtaining HRMS and processing ^{1}H and ^{13}C spectra for all the compounds.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO702436P

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